Supplementary Material (ESI) for Organic Letters

Synthesis of Biaryls via AlCl₃ Catalyzed Domino reaction Involving Cyclization, Dehydration followed by Oxidation

Tadigoppula Narender,* Satinath Sarkar, Kandikonda Rajendar and Srinivas Tiwari
Medicinal and Process Chemistry Division, Central Drug Research Institute (CSIR),
Lucknow-226001, U.P. India
(Fax: +915222623405; E-mail: t.narendra@cdri.res.in).

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General information

All reagents were purchased from commercial suppliers and used without further purification. IR spectra of the compounds were recorded on Perkin-Elmer AC-1 spectrometer. ¹H NMR spectra were run on Bruker Advance DPX 300 MHz spectrometer in CDCl₃ and TMS was used as internal standard. ESI mass spectra were recorded on JEOL SX 102/DA-6000. Silica gel 230-400 mesh was used as stationary phase to isolate the compounds.
General procedure (I) for preparation of mono alkenylation of ketones:

Ketone (4 mmol) was added drop wise by syringe to a stirred solution of sodium hydride (8 mmol) in dimethyl formamide (10 mL) at -20 °C. The resulting pale-yellow solution was stirred for 20 min at -20 °C, then prenyl bromide (8 mmol) was added drop wise by syringe. The reaction mixture was stirred for 20 min at this temperature, then the reaction flask was removed from the cooling bath and was allowed to reach to room temperature. The reaction mixture was stirred for 1 h at room temperature. Then reaction was quenched by adding ice-cold water and extracted three times with ether. Ether part was concentrated by rotary evaporation. The residue was purified by flash-column chromatography on silica gel using (ethyl acetate/hexane) as eluents to provide the desired product.

Spectroscopic data of mono alkenylated ketones:

5-methyl-1-phenylhex-4-en-1-one (2a). Following the general procedure I, 2a was prepared using acetophenone (500 mg, 4.16 mmol), sodium hydride (200 mg, 8.32 mmol), 3,3-dimethyl allyl bromide (1 ml, 8.32 mmol), and DMF (10 ml). The product Rf 0.74 (10% ethylacetate:hexane) was isolated as yellow oil 440 mg (56% yield) by flash-column chromatography on silica gel using (ethyl acetate/hexane, 2:98). IR (Neat) 3021, 2964, 2874, 2366, 1721, 1459, 1381, 1286, 1218, 1074, 1024, 761, 668 cm⁻¹. ¹H-NMR (300 MHz, CDCl₃) δ 7.92 (d, J=1.44Hz, 2H), 7.58-7.53 (m, 1H), 7.50-7.44 (m, 1H), 5.11-5.06 (m, 1H), 3.50-3.41 (m, 2H), 2.48-2.38 (m, 1H), 2.30-2.20 (m, 1H), 1.64 (s, 3H), 1.60 (s, 3H). ¹³C-NMR (75 MHz, CDCl₃), δ 204.0 (C=O), 137.5 (C), 133.4 (CH), 132.6 (C), 128.4 (2CH), 128.2 (2CH), 121.6 (CH), 47.1 (CH₂), 30.3 (CH₂), 25.7 (CH₃), 17.7 (CH₃). MS (ESI) m/z 189.2 (M+H).

1-(4-methoxyphenyl)-5-methylhex-4-en-1-one (2b). Following the general procedure I, 2b was prepared using p-methoxy acetophenone (500 mg, 3.3 mmol), sodium hydride (160 mg, 6.6 mmol), 3,3-dimethyl allyl bromide (0.8 ml, 6.6 mmol), and DMF (10 ml). The product Rf 0.64 (10% ethylacetate:hexane) was isolated as deep yellow oil 440 mg (58% yield) by flash-column chromatography on silica gel using (ethyl acetate/hexane, 4:96). IR (Neat) 3752, 3409, 2970, 2854, 2372, 2116, 1667, 1603, 1511, 1459, 1375, 1308, 1257, 1171, 1030, 842, 761, 698, 609 cm⁻¹. ¹H-NMR (300 MHz, CDCl₃) δ 7.92 (d, J=6.94Hz, 2H), 6.93 (d, J=8.63Hz, 2H), 5.07 (t, J=8.09Hz, 1H), 3.86 (s, 3H), 3.44-3.35 (m, 2H), 2.43-2.34 (m, 1H), 2.27-2.18 (m, 1H), 1.62 (s, 3H), 1.57 (s, 3H). ¹³C-NMR (75 MHz, CDCl₃), δ 202.6 (C=O), 163.1 (C), 133.3 (C), 132.2 (C), 130.6 (2CH), 121.7 (CH), 113.5 (2CH), 55.4 (CH₃), 46.1 (CH₂), 30.6 (CH₂), 25.6 (CH₃), 17.9 (CH₃). MS (ESI) m/z 219.1 (M+H).

1-(4-chlorophenyl)-5-methylhex-4-en-1-one (2c). Following the general procedure I, 2c prepared using p-chloro acetophenone (500 mg, 3.3 mmol), sodium hydride (160 mg, 6.6mmol), 3,3-dimethyl allyl bromide (0.8 ml, 6.6 mmol), and DMF (10 ml). The product Rf 0.70 (10% ethylacetate:hexane) was isolated as yellow oil 440 mg (61% yield) by flash-column chromatography on silica gel using (ethyl acetate/hexane, 3:97). IR (Neat) 3905, 3753, 3488, 3063, 2927, 2865, 2732, 2372, 2316, 1665, 1608, 1467, 1378, 1218, 1165, 1082, 1001, 885, 769, 699 cm⁻¹. ¹H-NMR (300 MHz, CDCl₃) δ 7.84 (d, J=8.54Hz, 2H), 7.74 (d, J=8.54Hz, 2H), 5.11 (t, J=6.25Hz, 1H), 3.49-3.40 (m, 2H), 2.54-2.41 (m, 1H), 1.64 (s, 3H), 1.60 (s, 3H).
2.34-2.24 (m, 1H), 1.68 (s, 3H), 1.63 (s, 3H). $^{13}$C-NMR (75 MHz, CDCl$_3$), $\delta$ 204.0 (C=O), 137.3 (C), 134.7 (C), 132.7 (C), 130.8 (2CH), 128.8 (2CH), 122.3 (CH), 48.1 (CH$_2$), 31.4 (CH$_2$), 26.7 (CH$_3$), 18.7 (CH$_3$). MS (ESI) m/z 223.7 (M+H).

5-methyl-1-p-tolylhex-4-en-1-one (2d). Following the general procedure I, 2d was prepared using p-methyl acetophenone (500 mg, 2.5 mmol), sodium hydride (150 mg, 5.0 mmol), 3,3-dimethyl allyl bromide (0.6 ml, 5.0 mmol), and DMF (10 ml). The product R$_f$ 0.76 (10% ethylacetate:hexane) was isolated as yellow oil 412 mg (53% yield) by flash-column chromatography on silica gel using (ethyl acetate/hexane, 2:98). IR (Neat) 3841, 3469, 3020, 2924, 2856, 2737, 2370, 1682, 1607, 1549, 1375, 1218, 1149, 1004, 868, 760, 688 cm$^{-1}$. $^1$H-NMR (300 MHz, CDCl$_3$) $\delta$ 7.53 (d, $J$=7.35Hz, 2H), 7.34 (d, $J$=8.43Hz, 2H), 5.09 (t, $J$=6.15Hz, 1H), 3.17-3.08 (m, 2H), 2.43 (s, 3H), 2.19-2.10 (m, 1H), 2.02-1.95 (m, 1H), 1.62 (s, 3H), 1.57 (s, 3H). $^{13}$C-NMR (75 MHz, CDCl$_3$), $\delta$ 203.0 (C=O), 136.8 (C), 134.2 (C), 132.3 (C), 130.3 (2CH), 128.3 (2CH), 121.9 (CH), 47.7 (CH$_2$), 30.9 (CH$_2$), 26.2 (CH$_3$), 20.2 (CH$_3$), 18.3 (CH$_3$). MS (ESI) m/z 203.1 (M+H).

1-(4-bromophenyl)-5-methylhex-4-en-1-one (2e). Following the general procedure I, 2e was prepared using p-bromo acetophenone (500 mg, 2.5 mmol), sodium hydride (150 mg, 5.0 mmol), 3,3-dimethyl allyl bromide (0.6 ml, 5.0 mmol), and DMF (10 ml). The product R$_f$ 0.72 (10% ethylacetate:hexane) was yellow oil 420 mg (63% yield) by flash-column chromatography on silica gel using (ethyl acetate/hexane, 3:97). IR (Neat) 3019, 2963, 2875, 2365, 1723, 1585, 1460, 1380, 1289, 1219, 1128, 1073, 761, 667 cm$^{-1}$. $^1$H-NMR (300 MHz, CDCl$_3$) $\delta$ 7.78 (d, $J$=7.43Hz, 2H), 7.59 (d, $J$=8.58Hz, 2H), 5.05 (t, $J$=6.25Hz, 1H), 3.43-3.34 (m, 2H), 2.72-2.63 (m, 1H), 2.45-2.35 (m, 1H), 1.62 (s, 3H), 1.57 (s, 3H). $^{13}$C-NMR (75 MHz, CDCl$_3$), $\delta$ 203.0 (C=O), 136.3 (C), 133.7 (C), 131.7 (2CH), 129.8 (2CH), 127.8 (C), 121.3 (CH), 47.1 (CH$_2$), 30.4 (CH$_2$), 25.7 (CH$_3$), 17.7 (CH$_3$). MS (ESI) m/z 268.1 (M+H).

1-(2,4-dimethylphenyl)-5-methylhex-4-en-1-one (2f). Following the general procedure I, 2f was prepared using 2,4-dimethylacetophenone (500 mg, 3.7 mmol), sodium hydride (200 mg, 7.4 mmol), 3,3-dimethyl allyl bromide (0.9 ml, 7.4 mmol), and DMF (10 ml). Deep yellow liquid crude product, which was not isolated.

6-methyl-3-phenylhept-5-en-2-one (5a). Following the general procedure I, 5a was prepared using phenyl acetone (4a) (500 mg, 3.73 mmol), sodium hydride (180 mg, 7.46 mmol), 3,3-dimethyl allyl bromide (0.9 ml, 7.46 mmol), and DMF (10 ml). The product R$_f$ 0.72 (10% ethylacetate:hexane) was isolated as yellow oil 420 mg (63% yield) by flash-column chromatography on silica gel using (ethyl acetate/hexane, 3:97). IR (Neat) 3019, 2963, 2875, 2365, 1723, 1585, 1460, 1380, 1289, 1219, 1128, 1073, 761, 667 cm$^{-1}$. $^1$H-NMR (300 MHz, CDCl$_3$) $\delta$ 7.78 (d, $J$=7.43Hz, 2H), 7.59 (d, $J$=8.58Hz, 2H), 5.05 (t, $J$=6.25Hz, 1H), 3.43-3.34 (m, 2H), 2.72-2.63 (m, 1H), 2.45-2.35 (m, 1H), 1.62 (s, 3H), 1.57 (s, 3H). $^{13}$C-NMR (75 MHz, CDCl$_3$), $\delta$ 203.0 (C=O), 136.3 (C), 133.7 (C), 131.7 (2CH), 129.8 (2CH), 127.8 (C), 121.3 (CH), 47.1 (CH$_2$), 30.4 (CH$_2$), 25.7 (CH$_3$), 17.7 (CH$_3$). MS (ESI) m/z 268.1 (M+H).
isolated as yellow oil 450 mg (60% yield) by flash-column chromatography on silica gel using (ethyl acetate/hexane, 3:97). IR (Neat) 3906, 3753, 3404, 3023, 2972, 2368, 2339, 1711, 1601, 1439, 1449, 1355, 1219, 1155, 1078, 1029, 760, 701, 668, cm\(^{-1}\). \(^1\)H-NMR (300 MHz, CDCl\(_3\)) \(\delta\) 7.32 (d, \(J=7.43\)Hz, 2H), 7.29-7.27 (m, 1H), 7.22 (d, \(J=6.85\)Hz, 2H), 5.00 (t, \(J=6.13\)Hz, 1H), 3.63 (t, \(J=7.20\)Hz, 1H), 2.78-2.69 (m, 1H), 2.41-2.32 (m, 1H), 2.07 (s, 3H), 1.63 (s, 3H), 1.55 (s, 3H). \(^1\)C-NMR (75 MHz, CDCl\(_3\)) \(\delta\) 208.5 (C=O), 138.7 (C), 133.3 (C), 128.7 (2CH), 128.3 (2CH), 127.1 (CH), 121.3 (CH), 59.9 (CH), 30.7 (CH\(_2\)), 29.1 (CH\(_3\)), 25.6 (CH\(_3\)), 17.7 (CH\(_3\)). MS (ESI) \(m/\zeta\) 203.0 (M+H).

3-(4-methoxyphenyl)-6-methylhept-5-en-2-one (5b). Following the general procedure I, 5b prepared using 4-methoxy phenyl acetone (4b) (500 mg, 4mmol), sodium hydride (200 mg, 8mmol), 3,3-dimethyl allyl bromide (1.1 ml, 8 mmol), and DMF (10 ml). The product \(R_f\) 0.68 (10% ethylacetate:hexane) was isolated as yellow oil 460 mg (66% yield) by flash-column chromatography on silica gel using (ethyl acetate/hexane, 4:96). IR (Neat) 3903, 3757, 3423, 3012, 2926, 2853, 2368, 1709, 1609, 1513, 1460, 1364, 1251, 1176, 1035, 830, 763, 671. cm\(^{-1}\). \(^1\)H-NMR (300 MHz, CDCl\(_3\)) \(\delta\) 7.15 (d, \(J=8.60\)Hz, 2H), 6.87 (d, \(J=8.60\)Hz, 2H), 5.03-4.97 (m, 1H), 3.80 (s, 3H), 3.59 (t, \(J=7.35\)Hz, 1H), 2.76-2.66 (m, 1H), 2.39-2.27 (m, 1H), 2.06 (s, 3H), 1.64 (s, 3H), 1.56 (s, 3H). \(^1\)C-NMR (75 MHz, CDCl\(_3\)) \(\delta\) 208.5 (C=O), 158.8 (C), 133.3 (C), 130.9 (C), 129.2 (2CH), 121.4 (CH), 114.2 (2CH), 58.9 (CH), 55.1 (CH\(_3\)), 30.7 (CH\(_2\)), 28.9 (CH\(_3\)), 25.6 (CH\(_3\)), 17.7 (CH\(_3\)). MS (ESI) \(m/\zeta\) 233.1 (M+H).

3-(3-chlorophenyl)-6-methylhept-5-en-2-one (5c). Following the general procedure I, 5c prepared using 3-chloro phenyl acetone (4c) (500 mg, 3 mmol), Sodium hydride (150 mg, 6 mmol), 3,3-dimethyl allyl bromide (0.7 ml, 6 mmol), and DMF (10 ml). The product \(R_f\) 0.70 (10% ethylacetate:hexane) was isolated as yellow oil 440 mg (63% yield) by flash-column chromatography on silica gel using (ethyl acetate/hexane, 3:97). IR (Neat) 3905, 3760, 3409, 2970, 2367, 1712, 1576, 1469, 1428, 1364, 1219, 1158, 1086, 957, 888, 765, 697 cm\(^{-1}\). \(^1\)H-NMR (300 MHz, CDCl\(_3\)) \(\delta\) 7.26-7.23 (m, 3H), 7.11-7.10 (m, 1H), 4.97 (t, \(J=6.35\)Hz, 1H), 3.61 (t, \(J=7.40\)Hz, 1H), 2.76-2.61 (m, 1H), 2.40-2.27 (m, 1H), 2.08 (s, 3H), 1.64 (s, 3H), 1.55 (s, 3H). \(^1\)C-NMR (75 MHz, CDCl\(_3\)) \(\delta\) 207.6 (C=O), 140.6 (C), 134.6 (C), 134.0 (C), 130.0 (CH), 128.4 (CH), 127.4 (CH), 126.4 (CH), 120.8 (CH), 59.4 (CH), 30.7 (CH\(_2\)), 29.3 (CH\(_3\)), 25.6 (CH\(_3\)), 17.7 (CH\(_3\)). MS (ESI) \(m/\zeta\) 237.7 (M+H).

3-(4-chlorophenyl)-6-methylhept-5-en-2-one (5d). Following the general procedure I, 5d was prepared using 4-chloro phenyl acetone (4d) (500 mg, 3 mmol), sodium hydride (150 mg, 6 mmol), 3,3-dimethyl allyl bromide (0.7 ml, 6 mmol), and DMF (10 ml). The product \(R_f\) 0.70 (10% ethylacetate:hexane) was isolated as yellow oil 440 mg (63% yield) by flash-column chromatography on silica gel using (ethyl acetate/hexane, 3:97). IR (Neat) 3903, 3760, 3309, 2983, 2362, 1710, 1469, 1422, 1368, 1216, 1148, 1080, 960, 745, 693 cm\(^{-1}\). \(^1\)H-NMR (300 MHz, CDCl\(_3\)) \(\delta\) 7.45 (d, \(J=8.67\)Hz, 2H), 7.18 (d, \(J=8.70\)Hz,
2H), 4.99 (t, J=6.33, 1H), 3.63 (t, J=7.38Hz, 1H), 2.76-2.63 (m, 1H), 2.42-2.32 (m, 1H), 2.10 (s, 3H), 1.66 (s, 3H), 1.57 (s, 3H). 13C-NMR (75 MHz, CDCl3) δ 208.6 (C=O), 141.5 (C), 135.3 (C), 134.7 (C), 130.7 (2CH), 128.1 (2CH), 121.5 (CH), 60.0 (CH), 31.4 (CH2), 30.0 (CH3), 26.3 (CH3), 18.5 (CH3).

6-methyl-3-p-tolylhept-5-en-2-one (5e). Following the general procedure I, 5e was prepared using 4-methyl phenyl acetone (4e) (500 mg, 3.3 mmol), sodium hydride (160 mg, 6.6 mmol), 3,3-dimethyl allyl bromide (0.8 ml, 6.6 mmol), and DMF (10 ml). The product Rf 0.72 (10% ethylacetate:hexane) was isolated as yellow oil 472 mg (65% yield) by flash-column chromatography on silica gel using (ethyl acetate/hexane,3:97). IR (Neat) 3905, 3741, 3460, 3022, 2982, 2922, 2845, 2743, 2380, 1705, 1608, 1515, 1452, 1376, 1220, 1145, 867, 763, 686 cm⁻¹. 1H-NMR (300 MHz, CDCl3) δ 7.16 (d, J=8.85Hz, 2H), 6.89 (d, J=8.85Hz, 2H), 5.01 (t, J=7.32, 1H), 3.60 (t, J=9.09Hz, 1H), 2.77-2.67 (m, 1H), 2.41-2.31 (m, 1H), 2.21 (s, 3H), 2.07 (s, 3H), 1.65 (s, 3H), 1.57 (s, 3H). 13C-NMR (75 MHz, CDCl3), δ 208.2 (C=O), 138.8 (C), 133.4 (C), 132.5 (C), 128.7 (2CH), 128.2 (2CH), 121.2 (CH), 57.5 (CH), 30.7 (CH2), 29.0 (CH3), 25.6 (CH3), 22.6 (CH3), 17.6 (CH3). MS (ESI) m/z 217.1 (M+H).

(Z)-3-(4-methoxyphenyl)-6,10-dimethylundeca-5,9-dien-2-one (7). Following the general procedure I, 7 using 4-methoxy phenyl acetone (4b) (500 mg, 4 mmol), sodium hydride (200 mg, 8 mmol), geranyl bromide (1.2 ml, 8 mmol), and DMF (10 ml). The product Rf 0.60 (10% ethylacetate:hexane) was isolated as yellow oil 460 mg (66% yield) by flash-column chromatography on silica gel using (ethyl acetate/hexane, 5:95). IR (Neat) 3476, 3423, 2935, 1708, 1608, 1511, 1451, 1251, 1175, 1032, 762 cm⁻¹. 1H-NMR (300 MHz, CDCl3) δ 7.13 (d, J=8.60Hz, 2H), 6.86 (d, J=8.60Hz, 2H), 5.01 (t, J=5.49Hz, 2H), 3.78 (s, 3H), 3.60-3.53 (m, 1H), 2.75-2.65 (m, 1H), 2.40-2.26 (m, 1H), 2.04-1.88 (m, 7H), 1.67 (s, 3H), 1.57 (s, 3H), 1.54 (s, 3H). 13C-NMR (75 MHz, CDCl3), δ 208.6 (C=O), 159.0 (C), 136.9 (C), 131.1 (C), 130.8 (C), 129.2 (2CH), 124.1 (CH), 121.4 (CH), 114.2 (2CH), 59.0 (CH), 55.2 (CH2), 39.8 (CH2), 30.6 (CH2), 29.0 (CH2), 26.6 (CH3), 25.6 (CH3), 17.6 (CH3), 16.0 (CH3). MS (ESI) m/z 301.2 (M+H).

5-methyl-1-(naphthalen-2-yl)hex-4-en-1-one (10). Following the general procedure I, 10 was prepared using 2-acetyl naphthalene 9 (500 mg, 3 mmol), sodium hydride (150 mg, 6 mmol), 3,3-dimethyl allyl bromide (0.7 ml, 6 mmol), and DMF (10 ml). The product Rf 0.70 (10% ethylacetate:hexane) was isolated as yellow oil 400 mg (57% yield) by flash-column chromatography on silica gel using (ethyl acetate/hexane, 3:97). IR (Neat) 3903, 3834, 3752, 3682, 3441, 2925, 2860, 2367, 1676, 1512, 1459,
1375, 1275, 1220, 864, 768, 672 cm⁻¹. ¹H-NMR (300 MHz, CDCl₃) δ 8.44 (s, 1H), 8.01-7.97 (m, 2H), 7.91-7.88 (m, 2H), 7.63-7.54 (m, 2H), 5.14 (t, J=6.90, 1H), 3.69-3.58 (m, 2H), 2.54-2.44 (m, 1H), 2.36-2.27 (m, 1H), 1.64 (s, 3H), 1.61 (s, 3H). ¹³C-NMR (75 MHz, CDCl₃), δ 203.1 (C=O), 142.1 (C), 134.8 (C), 133.3 (2C), 130.2 (CH), 128.8 (2CH), 128.2 (3CH), 125.7 (CH), 121.6 (CH), 51.0 (CH₂), 30.0 (CH₂), 25.7 (CH₃), 17.8 (CH₃). MS (ESI) m/z 239.3 (M+H).

2-(4-methoxybenzyl)-1-(4-methoxyphenyl)-5-methylhex-4-en-1-one (13). Following the general procedure I, 13 was prepared using 1,3-bis(4-methoxyphenyl)propan-1-one (12) (500 mg, 1.8 mmol), sodium hydride (100 mg, 3.6 mmol), 3,3-dimethyl allyl bromide (0.5 ml, 3.6 mmol), and DMF (10 ml). The product Rf 0.52 (10% ethylacetate:hexane) was isolated as yellow oil 420 mg (67% yield) by flash-column chromatography on silica gel using (ethyl acetate/hexane, 6:94). IR (Neat) 3905, 3752, 3416, 3017, 2931, 2842, 2364, 1688, 1601, 1512, 1458, 1373, 1304, 1274, 1219, 1173, 1033, 950, 839, 759, 669, 605. cm⁻¹. ¹H-NMR (300 MHz, CDCl₃) δ 7.86 (d, J=8.83Hz, 2H), 7.09 (d, J=8.60Hz, 2H), 6.88 (d, J=8.93Hz, 2H), 6.77 (d, J=8.60Hz, 2H), 5.11 (t, J=7.03Hz, 1H), 3.83 (s, 3H), 3.74 (s, 3H), 3.67 (t, J=7.04Hz, 1H), 3.09-3.02 (dd, J=13.71Hz, 7.89Hz, 1H), 2.79-2.72 (dd, J=13.90Hz, 6.20Hz, 1H), 2.48-2.38 (m, 1H), 2.30-2.21 (m, 1H), 1.64 (s, 3H), 1.55 (s, 3H). ¹³C-NMR (75 MHz, CDCl₃), δ 202.1 (C=O), 163.2 (C), 157.9 (C), 133.6 (C), 132.2 (2C), 130.4 (2CH), 129.9 (2CH), 121.3 (CH), 113.7 (2CH), 113.6 (2CH), 55.3 (CH₃), 55.1 (CH₃), 48.5 (C), 36.8 (CH₂), 31.0 (CH₂), 25.7 (CH₃), 17.8 (CH₃). MS (ESI) m/z 339.3 (M+H).

General procedure (II) for synthesis of Biaryl:

To a stirred solution of monoalketylated ketone (0.1 g) in dry dioxane (5 ml,) was added catalytic amount of AlCl₃ (20 mol%) at room temperature and stirred for 2.5-12 hours. The formation of biaryls was monitored by TLC and long range UV lamp (365 nm wave length). After dilution with moist ether (50 ml), the solution was washed with water (3x10 ml) to discharge the color. The combined ethereal solution obtained after extraction was dried over anhydrous Na₂SO₄ and evaporated under reduced pressure. The crude mixture was subjectd to flash-column chromatography on silica gel (ethyl acetate/hexane) to provide the desired product.

Spectroscopic data of Biaryls:

3-methylbiphenyl (3a). Following the general procedure II, 3a was prepared using 2a (100 mg) and AlCl₃. The product Rf 0.86 (10% ethylacetate:hexane) was isolated as yellow oil 52 mg (59% yield) by flash-column chromatography using (ethyl acetate/hexane, 0.5:99.5) as eluants. IR (Neat) 2960, 1612, 1486 cm⁻¹. ¹H-NMR (300 MHz, CDCl₃) δ 7.56-7.54 (m, 1H), 7.40-7.35 (m, 3H), 7.31-7.21 (m, 5H), 2.38 (s, 3H). ¹³C-NMR (75 MHz, CDCl₃), δ 141.4 (C), 141.3 (C), 138.3 (C), 128.7 (2CH), 128.7 (CH), 128.0 (CH), 128.0 (CH), 127.2 (CH), 127.2 (2CH), 124.3 (CH), 21.6 (CH₃). MS (ESI) m/z 169.1 (M+H). HRMS (ESI) calculated for C₁₃H₁₂, 169.0939 (M+H); found 169.1222.
4'-methoxy-3-methylbiphenyl (3b). Following the general procedure II, 3b was prepared using 2b (100 mg) and AlCl₃. The product Rₚ 0.78 (10% ethylacetate:hexane) was isolated as yellow oil 73 mg (80% yield) by flash-column chromatography using (ethyl acetate/hexane, 1.5:98.5) as eluants. IR (Neat) 2991, 2967, 1609, 1513, 1460 cm⁻¹. ¹H-NMR (300 MHz, CDCl₃) δ 7.60 (d, J=8.76Hz, 2H), 7.46-7.30 (m, 2H), 7.05 (d, J=8.76Hz, 2H), 3.19 (s, 3H), 2.49 (s, 3H). ¹³C-NMR (75 MHz, CDCl₃), δ 159.2 (C), 140.9 (C), 138.3 (C), 133.9 (C), 128.7 (CH), 128.2 (2CH), 127.6 (CH), 127.5 (CH), 123.9 (CH), 114.2 (2CH), 55.3 (CH₃), 21.6 (CH₃). MS (ESI) m/z 199.1 (M+H). HRMS (ESI) calculated for C₁₄H₁₄O, 199.1045 (M+H); found 199.1603 (M+H).

4'-chloro-3-methylbiphenyl (3c). Following the general procedure II, 3c was prepared using 2c (100 mg) and AlCl₃. The product Rₚ 0.80 (10% ethylacetate:hexane) was isolated as yellow oil 51 mg (56% yield) by flash-column chromatography using (ethyl acetate/hexane, 1:99) as eluants. IR (Neat) 2965, 1615, 1490, 755. cm⁻¹. ¹H-NMR (300 MHz, CDCl₃) δ 7.53 (d, J=8.49Hz, 2H), 7.37-7.28 (m, 3H), 7.13 (d, J=6.90Hz, 1H), 6.98 (d, J=8.76Hz, 2H), 2.44 (s, 3H). ¹³C-NMR (75 MHz, CDCl₃), δ 140.9 (C), 139.9 (C), 138.2 (C), 129.9 (CH), 128.6 (2CH), 128.2 (CH), 127.5 (CH), 127.4 (2CH), 124.9 (CH), 21.5 (CH₃). MS (ESI) m/z 204.0 (M+H). HRMS (ESI) calculated for C₁₃H₁₁Cl, 203.0549 (M+H); found 204.1445 (M+H).

3,4'-dimethylbiphenyl (3d). Following the general procedure II, 3d was prepared using 2d (100 mg) and AlCl₃. The product Rₚ 0.84 (10% ethylacetate:hexane) was isolated as yellow oil 27.9 mg (41% yield) by flash-column chromatography using (ethyl acetate/hexane, 0.5:99.5) as eluants. IR (Neat) 2983, 2963, 1488. cm⁻¹. ¹H-NMR (300 MHz, CDCl₃) δ 7.53 (d, J=8.49Hz, 2H), 7.37-7.28 (m, 4H), 2.46 (s, 3H), 2.44 (s, 3H). ¹³C-NMR (75 MHz, CDCl₃), δ 141.3 (C), 138.6 (C), 136.9 (C), 131.6 (2CH), 128.7 (CH), 127.9 (CH), 127.8 (2CH), 127.1 (2CH), 124.1 (CH), 21.6 (CH₃), 21.2 (CH₃). MS (ESI) m/z 183.1 (M+H). HRMS (ESI) calculated for C₁₄H₁₄, 183.1096 (M+H); found 183.0816 (M+H).

4'-bromo-3-methylbiphenyl (3e). Following the general procedure II, 3e was prepared using 2e (100 mg) and AlCl₃. The product Rₚ 0.82 (10% ethylacetate:hexane) was isolated as yellow oil 42 mg (45% yield) by flash-column chromatography using (ethyl acetate/hexane, 1:99) as eluants. IR (Neat) 2951, 2924, 1637, 1499, 696 cm⁻¹. ¹H-NMR (300 MHz, CDCl₃) δ 7.51 (d, J=8.01Hz, 2H), 7.41 (d, J=7.83Hz, 2H), 7.36-7.25 (m, 4H), 2.44 (s, 3H). ¹³C-NMR (75 MHz, CDCl₃), δ 148.5 (C), 142.6 (C), 138.2 (C), 133.1 (CH), 131.9 (CH), 131.6 (2CH), 128.8 (CH), 126.5 (2CH), 124.1 (C), 120.5 (CH), 21.6 (CH₃).
MS (ESI) m/z 248.1 (M+H). HRMS (ESI) calculated for C_{13}H_{11}Br, 247.0044 (M+H); found 248.1277 (M+H).

2,3',4-trimethylbiphenyl (3f). Following the general procedure II, 3f was prepared using crude mixture 2f (150 mg) and AlCl₃. The product Rₜ 0.66 (10% ethylacetate:hexane) was isolated as yellow oil 49 mg (54% yield) by flash-column chromatography using (ethyl acetate/hexane, 0.5:99.5) as eluants. IR (Neat) 2993, 2982, 2955, 1623, 1489 cm⁻¹. ¹H-NMR (300 MHz, CDCl₃) δ 7.54 (d, J=8.10Hz, 1H), 7.30-7.12 (m, 6H), 2.46 (s, 3H), 2.44(s, 3H), 2.40(s,3H). ¹³C-NMR (75 MHz, CDCl₃), δ 141.1 (C), 139.8 (C), 138.5 (C), 138.2 (C), 136.9 (CH), 133.8 (CH), 129.4 (CH), 128.6 (CH), 127.8 (CH), 127.0 (CH), 124.0 (CH), 21.5 (CH₃), 21.0 (CH₃), 20.1 (CH₃). MS (ESI) m/z 197.1 (M+H). HRMS (ESI) calculated for C_{15}H_{16}, 197.1252 (M+H); found 197.1230 (M+H).

2,4-dimethylbiphenyl (6a). Following the general procedure II, 6a prepared using 5a (100 mg) and AlCl₃. The product Rₜ 0.86 (10% ethylacetate:hexane) was isolated as yellow oil 65 mg (72% yield) by flash-column chromatography using (ethyl acetate/hexane, 0.5:99.5) as eluants. IR (Neat) 2924, 2862, 1647, 1483, 1449 cm⁻¹. ¹H-NMR (300 MHz, CDCl₃) δ 7.49-7.37 (m, 5H), 7.22-7.11 (m, 3H), 2.43 (s, 3H), 2.31 (s, 3H). ¹³C-NMR (75 MHz, CDCl₃), δ 142.1 (C), 139.2 (C), 136.9 (C), 135.1 (C), 131.1 (CH), 129.8 (CH), 129.3 (2CH), 128.1 (2CH), 126.6 (CH), 126.5(CH), 21.0(CH₃), 20.3(CH₃). MS (ESI) m/z 183.1 (M+H). HRMS (ESI) calculated for C_{14}H_{14}, 183.1096 (M+H); found 183.1412 (M+H).

4'-methoxy-2,4-dimethylbiphenyl (6b). Following the general procedure II, 6b was prepared using 5b (100 mg) and AlCl₃. The product Rₜ 0.80 (10% ethylacetate:hexane) was isolated as yellow oil 72 mg (79% yield) by flash-column chromatography using (ethyl acetate/hexane, 1:99) as eluants. IR (Neat) 2921, 2852, 1646, 1462 cm⁻¹. ¹H-NMR (300 MHz, CDCl₃) δ 7.28-7.25 (m, 2H), 7.16-7.06 (m, 3H), 6.97 (d, J=8.73Hz, 2H), 3.88 (s, 3H), 2.39 (s, 3H), 2.28 (s, 3H). ¹³C-NMR (75 MHz, CDCl₃), δ 158.3 (C), 138.7 (C), 136.6 (C), 131.1 (CH), 130.3 (2CH+2C), 129.8 (CH), 126.5 (CH), 113.4 (2CH), 55.2 (CH₃), 21.1 (CH₃), 20.5 (CH₃). MS (ESI) m/z 213.1 (M+H). HRMS (ESI) calculated for C_{15}H_{16}O, 213.1277 (M+H); found 213.1277 (M+H).

3'-chloro-2,4-dimethylbiphenyl (6c). Following the general procedure II, 6c was prepared using 6b (100 mg) and AlCl₃. The product Rₜ 0.82 (10% ethylacetate:hexane) was isolated as yellow oil 61 mg (72% yield) by flash-column chromatography using (ethyl acetate/hexane, 1:99) as eluants. IR (Neat)
4'-chloro-2,4-dimethylbiphenyl (6d). Following the general procedure II, 6d was prepared using 5d (100 mg) and AlCl₃. The product Rₜ 0.82 (10% ethylacetate:hexane) was isolated as yellow oil 63 mg (69% yield) by flash-column chromatography using (ethyl acetate/hexane, 1:99) as eluants. IR (Neat) 2935, 2732, 1655, 1447, 776 cm⁻¹. ¹H-NMR (300 MHz, CDCl₃) δ 7.54 (d, J=8.67Hz, 2H), 7.38-7.29 (m, 3H), 7.14 (d, J=8.67Hz, 2H), 2.43 (s, 3H), 2.33 (s, 3H). ¹³C-NMR (75 MHz, CDCl₃), δ 143.9 (C), 137.8 (C), 135.0 (C), 134.0 (C), 131.3 (CH), 129.4 (2CH), 127.5 (2CH), 126.8 (CH), 21.1 (CH₃), 20.3 (CH₃). MS (ESI) m/z 218.2 (M+H). HRMS (ESI) calculated for C₁₄H₁₃Cl 217.0706 (M+H); found 218.0730 (M+H).

2,4,4'-trimethylbiphenyl (6e). Following the general procedure II, 6e prepared using 5e (100 mg) and AlCl₃. The product Rₜ 0.86 (10% ethylacetate:hexane) was isolated as yellow oil 67 mg (74% yield) by flash-column chromatography using (ethyl acetate/hexane, 0.5:99.5) as eluants. IR (Neat) 2993, 2985, 2965, 1623, 1489 cm⁻¹. ¹H-NMR (300 MHz, CDCl₃) δ 7.30 (d, J=8.64Hz, 2H), 7.21 (s, 1H), 6.99-6.97 (m, 2H), 3.88 (s, 3H), 2.81 (t, J=6.09Hz, 2H), 2.24 (s, 3H), 1.93-1.68 (m, 6H), 1.32 (s, 3H), 1.29 (s, 3H). ¹³C-NMR (75 MHz, CDCl₃), δ 158.7 (C), 143.7 (C), 139.6 (C), 135.3 (C), 135.0 (C), 132.7 (C), 131.1 (CH), 130.6 (2CH), 128.5 (CH), 113.7 (2CH), 55.6 (CH₃), 39.7 (CH₂), 33.9 (C), 32.2 (CH₃), 30.6 (CH₂), 30.1 (CH₃), 20.2 (CH₃), 20.1 (CH₃). MS (ESI) m/z 197.2 (M+H). HRMS (ESI) calculated for C₁₅H₁₆ 197.1252 (M+H); found 197.2270 (M+H).

7-(4-methoxyphenyl)-1,1,6-trimethyl-1,2,3,4-tetrahydronaphthalene (8). Following the general procedure II, 8 was prepared using 7 (100 mg) and AlCl₃. The product Rₜ 0.81 (10% ethylacetate:hexane) was isolated as yellow oil 49.2 mg (53% yield) by flash-column chromatography using (ethyl acetate/hexane, 1:99) as eluants. IR (Neat) 2961, 2874, 1601, 1461, 1285, 1128, 1073, 759 cm⁻¹. ¹H-NMR (300 MHz, CDCl₃) δ 7.29 (d, J=8.67Hz, 2H), 7.21 (s, 1H), 6.99-6.97 (m, 2H), 3.88 (s, 3H), 2.81 (t, J=6.09Hz, 2H), 2.24 (s, 3H), 1.93-1.68 (m, 6H), 1.32 (s, 3H), 1.29 (s, 3H). ¹³C-NMR (75 MHz, CDCl₃), δ 158.7 (C), 143.7 (C), 139.6 (C), 135.3 (C), 135.0 (C), 132.7 (C), 131.1 (CH), 130.6 (2CH), 128.5 (CH), 113.7 (2CH), 55.6 (CH₃), 39.7 (CH₂), 33.9 (C), 32.2 (CH₃), 30.6 (CH₂), 30.1 (CH₃), 20.2 (CH₃), 20.1 (CH₃). MS (ESI) m/z 281.1 (M+H). HRMS (ESI) calculated for C₂₀H₂₅O 281.1827 (M+H); found 281.1054 (M+H).
2-m-tolylnaphthalene (11). Following the general procedure II, 11 was prepared using 10 (100 mg) and AlCl₃. The product Rf 0.82 (10% ethylacetate:hexane) was isolated as yellow oil 61.6 mg (67% yield) by flash-column chromatography using (ethyl acetate/hexane, 1:99) as eluants. IR (Neat) 2924, 2855, 1602, 1457, 1217 cm⁻¹. ¹H-NMR (300 MHz, CDCl₃) δ 8.07 (s, 1H), 7.95-7.88 (m, 3H), 7.79-7.76 (m, 2H), 7.58-7.50 (m, 3H), 7.41 (t, J=7.63Hz, 1H), 7.25-7.17 (m, 1H), 2.51 (3H). ¹³C-NMR (75 MHz, CDCl₃), δ 141.2 (C), 138.8 (C), 138.5 (C), 133.8 (C), 132.7 (C), 128.9 (CH), 128.4 (CH), 128.3 (CH), 128.2 (CH), 127.7 (CH), 126.3 (CH), 125.9 (CH), 125.9 (CH), 125.8 (CH), 124.7 (CH), 21.7 (CH₃). MS (ESI) m/z 219.3 (M+H). HRMS (ESI) calculated for C₁₇H₁₄, 219.1096 (M+H); found 219.3020 (M+H).

4'-methoxy-2-(4-methoxybenzyl)-5-methylbiphenyl (14). Following the general procedure II, 14 was prepared using 13 (100 mg) and AlCl₃. The product Rf 0.74 (10% ethylacetate:hexane) was isolated as yellow oil 68.2 mg (73% yield) by flash-column chromatography using (ethyl acetate/hexane, 2:98) as eluants. IR (Neat) 2961, 2872, 1607, 1459, 1285 cm⁻¹. ¹H-NMR (300 MHz, CDCl₃) δ 7.19 (d, J=8.64Hz, 2H), 7.09 (d, J=4.55Hz, 3H), 6.93-6.90 (m, 4H), 6.77 (d, J=8.64Hz, 2H), 3.87 (s, 2H), 3.86 (s, 3H), 3.78 (s, 3H), 2.37 (s, 3H). ¹³C-NMR (75 MHz, CDCl₃), δ 158.6 (C), 157.7 (C), 141.6 (C), 135.8 (C), 135.5 (C), 134.3 (C), 133.9 (C), 131.0 (CH), 130.3 (2CH), 130.1 (CH), 129.7 (2CH), 127.9 (CH), 113.7 (2CH), 113.4 (2CH), 55.3 (CH₃), 55.2 (CH₃), 37.8 (CH₂), 20.9 (CH₃). MS (ESI) m/z 319.1 (M+H). HRMS (ESI) calculated for C₂₂H₂₂O₂, 319.1620 (M+H); found 319.1603 (M+H).
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